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## RESEARCH ARTICLE

# A cautionary note on the effects of laboratory air contaminants on ambient ionization mass spectrometry measurements

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**Rationale:** Ambient ionization mass spectrometry methods are convenient, sensitive and require little sample preparation. However, they are susceptible to species present in air surrounding the mass spectrometer. This study identifies some challenges associated with the potential impacts of indoor air contaminants on ionization and analysis involving open-air methods.

**Methods:** Unexpected effects of volatile organic compounds (VOCs) from floor maintenance activities on ambient ionization mass spectrometry were studied using three different ambient ionization techniques. Extractive electrospray ionization (EESI), direct analysis in real time (DART) and ionization by piezoelectric direct discharge (PDD) plasma were demonstrated in this study to be affected by indoor air contaminants. Identification of contaminant vapors was verified by comparison with standards using EESI-MS/MS product ion scans.

**Results:** Emissions of diethylene glycol monoethyl ether and ethylene glycol monobutyl ether are identified from floor stripping and waxing solutions using three ambient ionization mass spectrometry techniques. These unexpected indoor air contaminants are capable of more than 75% ion suppression of target analytes due to their high volatility, proton affinity and solubility compared with the target analytes. The contaminant vapors are also shown to form adducts with one of the target analytes.

**Conclusions:** The common practice in MS analysis of subtracting a background air spectrum may not be appropriate if the presence of ionizable air contaminants alters the spectrum in unexpected ways. For example, VOCs released into air from floor stripping and waxing are capable of causing ion suppression of target analytes.

## 1 | INTRODUCTION

Ambient ionization mass spectrometry techniques use ionization in open laboratory air to generate mass spectra of complex mixtures. Over 40 different types of ambient ionization techniques have been developed in the past decade.<sup>1-22</sup> Some of these methods include atmospheric solids analysis probe (ASAP),<sup>23</sup> direct analysis in real time (DART),<sup>24,25</sup> desorption electrospray ionization (DESI)<sup>26,27</sup> and extractive electrospray ionization (EESI).<sup>28</sup>

Ambient ionization methods offer many advantages, while drawing on more conventional ionization mechanisms. For example, EESI utilizes solvent droplets held at high potential, as does conventional electrospray ionization (ESI). However, in EESI the sample flow intersects the charged solvent droplets at the mass spectrometer inlet in open air, removing the need for sample preparation steps. Ambient ionization methods can be applied to different types of

samples,<sup>2-10,27-32</sup> including solids, liquids, gases, or analytes adsorbed on defined solid substrates, and they can also be used for imaging purposes. These techniques can be applied directly to the original medium or to *in situ* samples such as suspended particles<sup>33-37</sup> or plant leaves,<sup>38</sup> avoiding many of the uncertainties and challenges associated with solvent extraction, and sample preparation. In addition, open-air ionization is carried out very close to the mass spectrometer inlet (or directly within the inlet for matrix-assisted ionization),<sup>6,21</sup> minimizing sampling line artifacts and carry-over from previous experiments.

The relatively high concentration of water vapor (proton affinity (PA) = 691 kJ mol<sup>-1</sup>)<sup>39</sup> in ambient air is often utilized to generate ionized clusters of water [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> needed for protonation of analytes in ambient ionization techniques.<sup>1,5,17,40</sup> However, ionization under ambient conditions often also generates ions from other species present in the air. A classic example is ammonia (NH<sub>3</sub>), which is

ubiquitous in indoor air and comes from a number of sources including human breath where concentrations can range from 50 ppb to several hundred ppb.<sup>41,42</sup> Although ammonia concentrations in laboratory air are generally much lower than those of water vapor, the PA of ammonia is higher (853.6 kJ mol<sup>-1</sup>),<sup>39</sup> which results in the ionization of even trace levels of ammonia. As a result, many analytes form adducts with NH<sub>4</sub><sup>+</sup>, causing peaks that correspond to [M + NH<sub>4</sub>]<sup>+</sup> to appear in the mass spectra, in addition to the [M + H]<sup>+</sup> peaks. It is nearly impossible to eliminate ammonia from laboratories, but the presence of ammoniated adducts has proven to be useful in analyte identification.<sup>1</sup> In some cases, addition of reagents<sup>27,43-48</sup> provides promising solutions to selective analysis of target analytes in a high background laboratory environment. It has also been suggested that constraints on the ionization region would be helpful in minimizing ambient species.<sup>29,43</sup>

An important intersection of the increasing application of ambient ionization techniques is with the large body of research on indoor air quality. Indeed, indoor air has been reported to be rich in volatile organic compounds (VOCs),<sup>49-56</sup> many of which can be readily ionized. For example, volatile polydimethylsiloxanes present in ambient air have been measured as contaminants using nanoelectrospray analysis.<sup>57</sup> Acetone, which is a common trace species in the laboratory environment, and emissions from industrial materials used during the building maintenance and renovations are other examples.<sup>24,40,55</sup> The appearance of such trace species in mass spectra is commonly addressed by subtraction of a background mass spectrum of air (or other mass spectrum containing no analyte) from the sample spectrum or by the use of a large curtain gas flow to decrease neutral contaminants.<sup>58</sup> However, in an open-air configuration, these background contaminants can be substantial, can vary with time and can participate in ionization. This affects both qualitative and quantitative identification of analyte species and may be especially severe in indoor air environments where concentrations can be more elevated than in outdoor air.<sup>50-53,59</sup>

The effects of indoor air contaminants are addressed in this study using three ambient ionization techniques: EESI, DART and ionization by piezoelectric direct discharge (PDD) plasma.<sup>60</sup> These three different ionization techniques have important similarities that result in similar mass spectra for the same analytes.

While the ionization mechanism of EESI is not completely understood,<sup>1,61-63</sup> it is accepted that the charged solvent droplets from an ESI capillary interact with the analyte, introduced as a separate flow, in such a way that at least some of the analyte is extracted and forms ions that directly enter the mass spectrometer. EESI is a soft ionization technique, which in positive ion mode predominantly forms [M + H]<sup>+</sup> ions. The analyte ion signal intensity is dependent on the analyte solubility, concentration and proton affinity (in positive ion mode), assuming that the experimental configuration is constant.<sup>2,7,13,15,34,61,62</sup>

DART ionization is similar to atmospheric pressure chemical ionization (APCI). However, the initial ion formation in DART is based on Penning ionization,<sup>64</sup> where a metastable neutral gas (usually generated from He) interacts with atmospheric water vapor to produce positive ions (H<sub>3</sub>O<sup>+</sup> and its water clusters) and electrons. This is followed by proton transfer to the analyte giving [M + H]<sup>+</sup> ions. It is

also common to see [M + NH<sub>4</sub>]<sup>+</sup> and M<sup>+</sup> ions in DART-MS. The mechanism of DART ionization and its applications are described in detail by Domin and Cody.<sup>1</sup>

Li et al.<sup>60</sup> described a new technique called relay ESI, in which a PDD plasma was used as the primary ion source. This PDD plasma ionization method has been adapted here as an open-air ionization technique. The PDD plasma ionization works on the principle of piezoelectricity.<sup>65</sup> A slow squeeze of the PDD plasma generator trigger causes a compression of a piezoelectric crystal which generates potentials on the order of 10 kV<sup>66</sup> and typically a few μA<sup>60</sup> of current that generates ions in ambient air. The device does not contain any other energy source. When the trigger is slowly squeezed, a stream of positive ions is generated that interacts with the sample, resulting in [M + H]<sup>+</sup> ions of the analyte. Negative ions are generated during travel of the trigger back to its original position.

We report here the effects of building maintenance activities and associated VOCs on MS analyses using EESI, DART and PDD plasma ionization methods. There is a substantial impact of the floor treatment on the mass spectra, including significant analyte ion suppression as well as new adduct formation. Such effects are likely to be important as the applications of ambient ionization mass spectrometry in indoor air environments increase.

## 2 | EXPERIMENTAL

### 2.1 | Extractive electrospray ionization (EESI)

The apparatus for EESI used in these studies is described in detail elsewhere.<sup>37</sup> Briefly, a solution of 0.2% (v/v) formic acid (Certified ACS (88%); Fisher Scientific, Huntington Beach, CA, USA) prepared in 1:1 (v/v) methanol (ACS grade; Sigma-Aldrich, St Louis, MO, USA) and water (18 MΩ-cm, MilliQ; Millipore Corp., Temecula, CA, USA) was injected at 60 μL h<sup>-1</sup> from a syringe pump (NE 1000; New Era Pump Systems Inc., Farmingdale, NY, USA) into a 100 μm ID silica capillary (IDEX Health and Science, Rohnert Park, CA, USA). The end of the capillary was located ~1 cm away from the curtain plate of the triple quadrupole mass spectrometer (API-300; AB Sciex, Concord, ON, Canada). The curtain plate was maintained at a constant voltage of +1 kV. The solvent was subjected to a +4 kV potential from an external power supply (model 248; Keithley, Beaverton, OR, USA) to generate charged solvent droplets. The sample flow was introduced through a separate ¼" Teflon line, placed at ~45° angle to the solvent capillary which was also located ~1 cm from the curtain plate. The mass spectra were collected using Analyst software (AB Sciex). Mass spectra were collected every 3.5 s in positive ion mode (*m/z* 30–1000) and are reported as 5-min averages (100 spectra in total). Mass calibration of the instrument was performed using conventional ESI-MS with a standard calibration mixture of poly(ethylene glycol) with an average molecular weight (MW) of 200 Da (PEG-200; Sigma-Aldrich).

EESI-MS was applied to analyze pentanedioic acid particles before and after the floor treatment. Pentanedioic acid was dissolved in water to make a 4.3 mM solution. This solution was atomized using a constant flow atomizer (model 3076; TSI, Shoreview, MN, USA)

with nitrogen as the carrier gas (99.999%; Praxair, Inc., Santa Ana, CA, USA) at 30 psi backing pressure. The atomized pentanedioic acid aerosol particles were dried using two TSI diffusion driers (model 3062, desiccant: silica gel beads; Letica Corp., Sloan, NV, USA) connected in series. The size distributions of the particles were measured using a scanning mobility particle sizer (SMPS, TSI) composed of a differential mobility analyzer (model 3081) and a condensation particle counter (model 3025A) before and after EESI-MS experiments. A flow of 0.3 L min<sup>-1</sup> from the particle stream (total flow rate of 1.7 L min<sup>-1</sup>) was directed to the inlet of the SMPS (sheath air flow rate of 3 L min<sup>-1</sup>).

Analysis of gaseous samples was performed by EESI-MS without the use of the sample line by introducing headspace vapors into the region between the charged solvent droplet stream and the curtain plate. This was done for the vapor phase of *n*-butylamine, isopropyl alcohol, floor treatment solutions and pure glycol ether standards. The alignment of the sample line and the solvent capillary was optimized using the total ion count of the background spectrum and the intensity at *m/z* 65 of the methanol solvent [2M + H]<sup>+</sup> peak at the beginning of each experiment. The variability in the daily peak intensities was within ±20%.

## 2.2 | Direct analysis in real time (DART)

DART-MS measurements were performed using a triple quadrupole mass spectrometer (Xevo TQ-S; Waters, Milford, MA, USA) equipped with a commercial DART ion source (DART SVP with Vapor® interface; IonSense, Inc., Saugus, MA, USA). The DART ion source was operated at room temperature with a grid electrode voltage of 350 V and helium (99.999%; Praxair, Inc.) at a flow rate of 3.1 L min<sup>-1</sup>. Mass spectra were collected and analyzed using MassLynx

software (Waters). They were collected in positive ion mode (*m/z* 30–500) every second and are reported as 1-min averages (60 spectra in total).

## 2.3 | Ionization by piezoelectric direct discharge (PDD) plasma

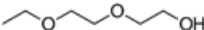
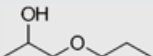
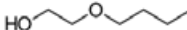
A hand-held piezoelectric discharge plasma generator (Milty Zerostat 3 anti-static gun; Armour Home, Bishops Stortford, UK) was used to generate ions at the Xevo TQ-S mass spectrometer inlet. In this case the DART-SVP probe was removed and the PDD plasma generator was used instead. For this study, the PDD plasma generator was applied to laboratory air and the headspace vapors to generate a single mass spectrum in positive ion mode (*m/z* 30–500). Typically, the PDD plasma generator was held ~5 cm away from the entrance of the mass spectrometer, which resulted in a charge of 1.5 Coulomb per cycle by each squeeze. The mass spectra were collected and analyzed using MassLynx software.

## 2.4 | Analytes

Standards for diethylene glycol monoethyl ether (99%, CAS # 111-90-0; TCI Chemicals, Portland, OR, USA), ethylene glycol monobutyl ether (99%, CAS # 111-76-2; TCI Chemicals), and propylene glycol *n*-propyl ether (98.5%, CAS # 1569-01-3; Sigma-Aldrich) were used as received. Isopropyl alcohol (ACS grade, CAS # 67-63-0; Macron Fine Chemicals, Center Valley, PA, USA), *n*-butylamine (99.5%, CAS # 109-73-9; Sigma-Aldrich) and pentanedioic acid (99%, CAS # 110-94-1; Sigma-Aldrich) were also used as received.

The building manager reported that the floor treatment was carried out using 'Alpha HP multi-surface cleaner' (Diversey, Inc., Racine, WI,

**TABLE 1** Composition of the floor stripping and waxing solutions<sup>a</sup> and additional compounds identified in this study

Sample	Composition <sup>b</sup>	MW (Da)	Structure <sup>c</sup>
Waxing solution <sup>d</sup>	Diethylene glycol monoethyl ether (DEGMEE) <i>2-(2-Ethoxyethoxy)ethanol</i>	134	
	Texanol <i>2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate</i>	216	-
	Acrylic acid polymer	-	-
	Zinc oxide	81	-
Stripping solution <sup>e</sup>	Tri( <i>n</i> -butoxyethyl) phosphate	398	-
	Propylene glycol <i>n</i> -propyl ether (PGPE) <i>1-Propoxy-2-propanol</i>	118	
	Dodecylbenzene sulfonic acid	326	-
	Ethoxylated linear alcohols	-	-
Additional compounds <sup>f</sup>	Hydrogen peroxide	34	-
	Ethylene glycol monobutyl ether (EGMBE) <i>2-Butoxyethanol</i>	118	
	Ammonia <sup>g</sup>	17	NH <sub>3</sub>

<sup>a</sup>Manufacturer's specifications.

<sup>b</sup>IUPAC names are italicized.

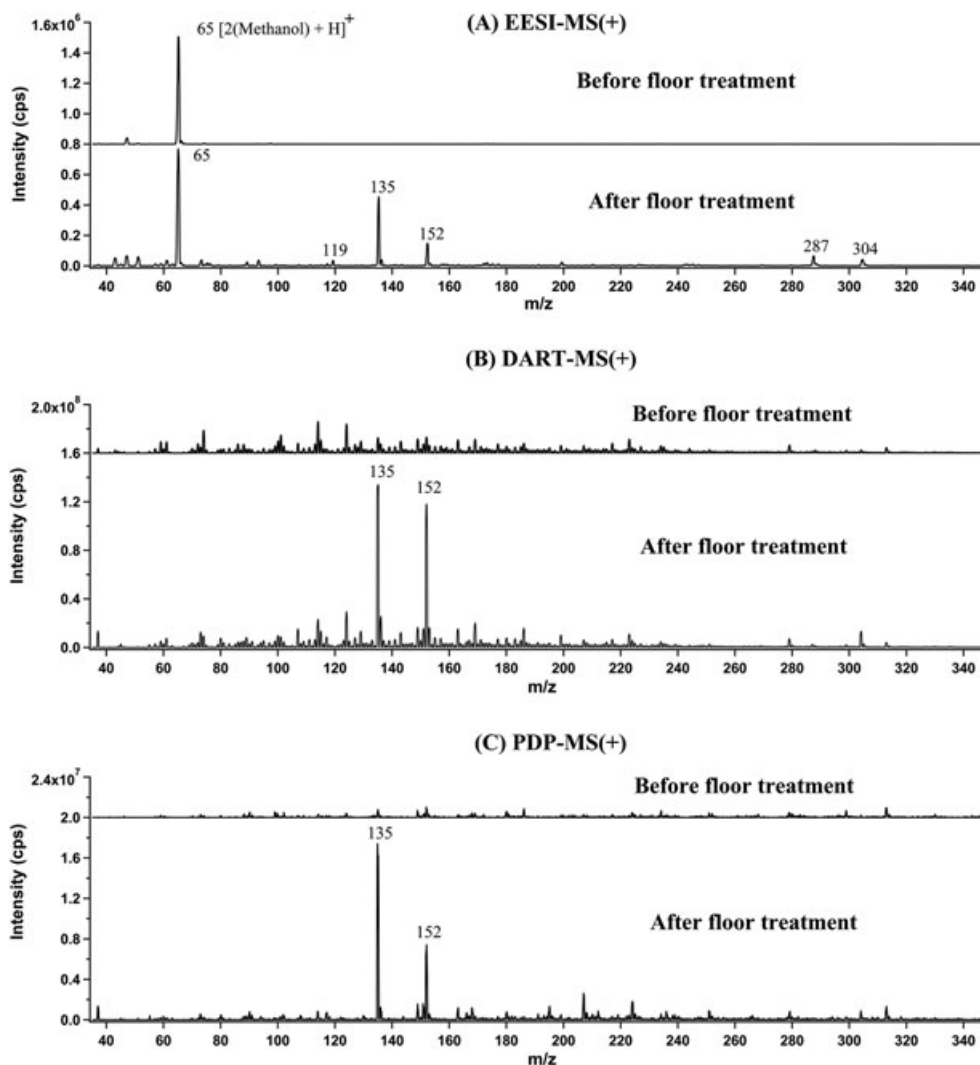
<sup>c</sup>Only the structures of the target compounds have been provided.

<sup>d</sup>Floor Star Floor Finish' (WAXIE Sanitary Supply).

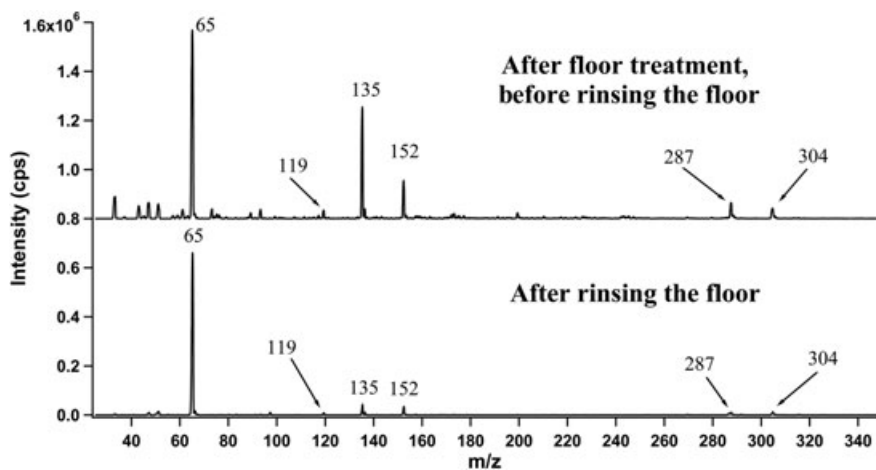
<sup>e</sup>'Alpha HP multi-surface cleaner' (Diversey, Inc.).

<sup>f</sup>Not listed in manufacturer's ingredients.

<sup>g</sup>Measured using ion chromatography, see text.



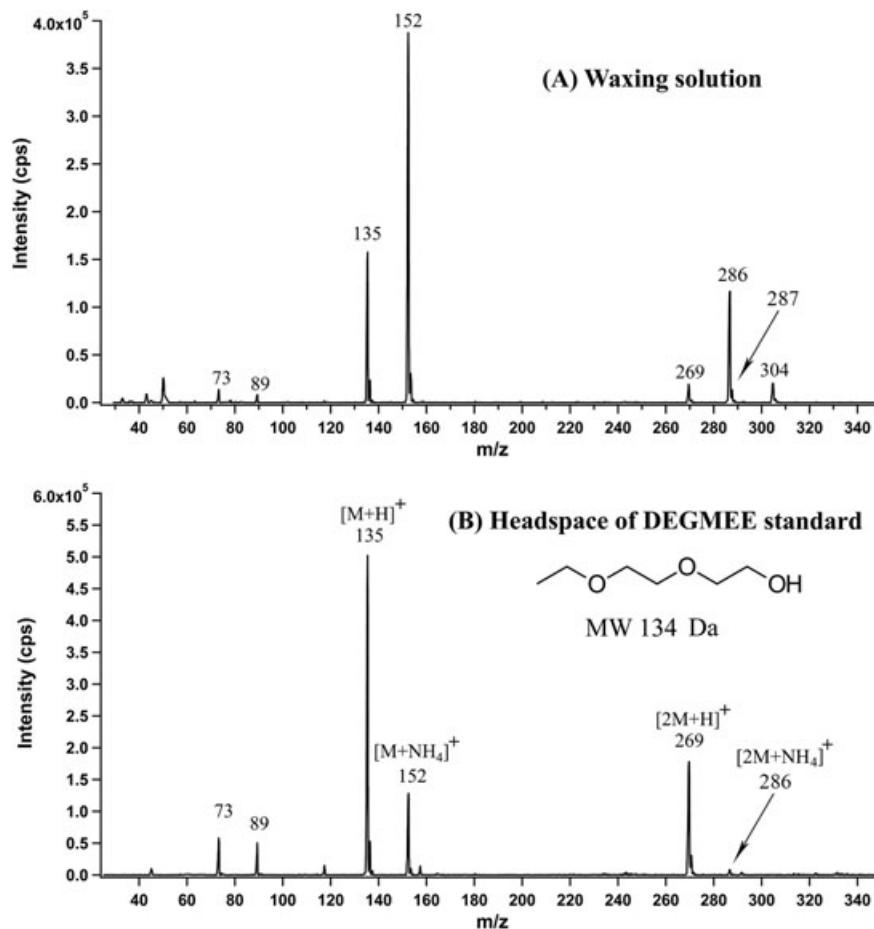
**FIGURE 1** Mass spectra of laboratory air, before and after floor treatment, measured by three techniques: A, EESI-MS(+); B, DART-MS(+); and C, PDP plasma ionization MS(+). The intensities are absolute and the top traces are vertically offset for clarity



**FIGURE 2** EESI-MS(+) spectra showing the effects of rinsing the floor with 18 MΩ-cm water. The intensities are absolute and the top trace is vertically offset for clarity

USA) as the stripping solution (to remove stains) and 'Floor Star Floor Finish' manufactured by WAXIE Sanitary Supply (Santa Ana, CA, USA) as the waxing solution. The reported composition of these solutions are given in Table 1. Ammonia was also shown to be present in the wax solution by ion chromatography analysis (Dionex ICS-1100;

Thermo Scientific, Sunnyvale, CA, USA). The separation was performed on an IonPac CS16 analytical column (Thermo Electron, West Palm Beach, FL, USA) kept at 40°C using the auto-suppression recycle mode (Dionex CERS 500 suppressor; Thermo Electron). The eluent was a 1:10 dilution of a 0.5 M oxalic acid commercial solution



**FIGURE 3** Solvent-subtracted EESI-MS(+) spectra of: A, the headspace of the waxing solution and B, the headspace vapor of an authentic liquid DEGMEE standard. The relative intensities of  $m/z$  135 to  $m/z$  152 vary due to the presence of ammonia in the wax solution

(Fisher Scientific, Houston, TX, USA) flowing at a rate of  $1 \text{ mL min}^{-1}$ . The retention time for the ammonium ion ( $\text{NH}_4^+$ ) from the wax solution matched that of an authentic standard solution. Floor treatment occurred in many laboratories throughout the building including that containing the AB Sciex API-300 mass spectrometer, over a period of 2 weeks, but not the floor housing the Waters TQ-S mass spectrometer.

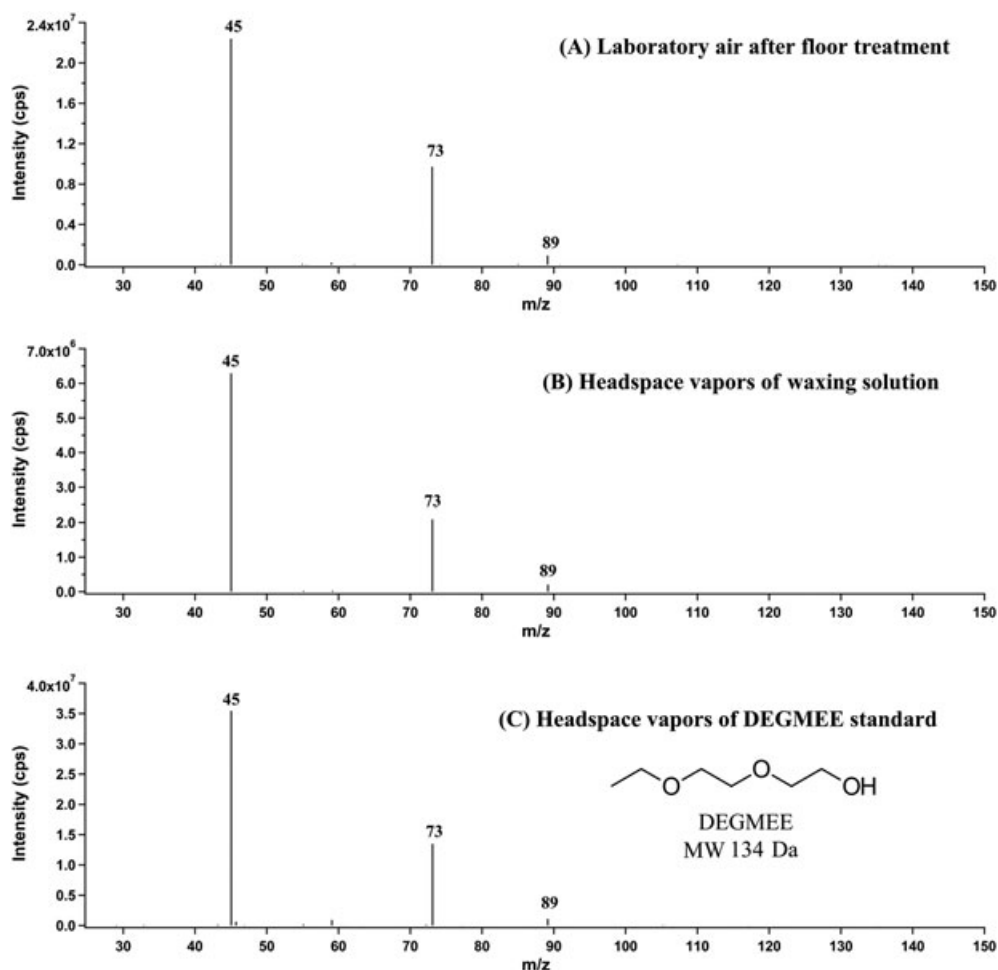
### 3 | RESULTS AND DISCUSSION

Typical EESI, DART and PDD plasma ionization positive ion mass spectra of laboratory air before and after the floor treatment are shown in Figure 1. All three ambient ionization techniques produced similar mass spectra, as expected given that  $[\text{M} + \text{H}]^+$  ions are the primary ions generated in each technique, with the exception of the peak at  $m/z$  65 in the EESI-MS spectra which is the  $[2\text{M} + \text{H}]^+$  ion from the methanol present in the EESI solvent. All three techniques showed the presence of significant new peaks at  $m/z$  135 and 152 after the floor treatment. The presence of these peaks in DART-MS operated at room temperature suggested they were formed from highly volatile species. The appearance of the same peaks using different instruments located on two different floors of the building suggested that there was a widespread source rather than contamination of the analyte delivery systems or contaminants in the different mass spectrometers or ionization regions.

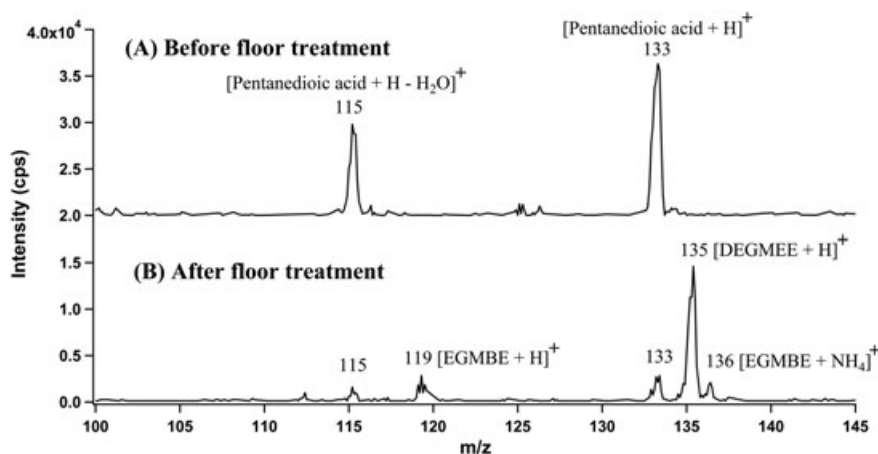
To further test if the floor treatment was responsible for the new peaks, the floor was rinsed with  $18 \text{ M}\Omega\text{-cm}$  water and allowed to dry. Figure 2 shows that the intensity of the peaks at  $m/z$  135 and 152 decreased by about an order of magnitude after rinsing, supporting the floor treatment as the source of the new species. Note that the laboratory in which DART and PDD plasma mass spectra were collected did not receive any floor treatment, yet still exhibited significant contaminant peaks due to sources throughout the building air venting system (Figures 1B and 1C). The results described below are reported for EESI, but were also observed using DART and PDD plasma ionization.

To determine that these new peaks were, in fact, due to the floor waxing, a sample of the headspace of the floor wax solution was analyzed using EESI-MS. Figure 3A shows the solvent-subtracted EESI-MS(+) spectrum of the headspace of the floor waxing solution. Major peaks are seen at  $m/z$  135, 152 and 286. The relative intensities are different from those of the laboratory air samples (Figure 2A) for reasons discussed later. Smaller peaks at  $m/z$  287 and 304 in the laboratory air sample (Figure 1A) are also present in the headspace of the floor waxing solution (Figure 3A), along with a minor peak at  $m/z$  269.

A major component of the floor waxing solution is diethylene glycol monoethyl ether (DEGMEE, MW 134 Da). Figure 3B shows the solvent-subtracted EESI-MS(+) spectrum of the headspace above a liquid sample of DEGMEE standard. Peaks at  $m/z$  135 and 152 were both observed, corresponding to the  $[\text{M} + \text{H}]^+$  and the  $[\text{M} + \text{NH}_4]^+$  ions of DEGMEE, respectively. The assignment of these peaks to DEGMEE



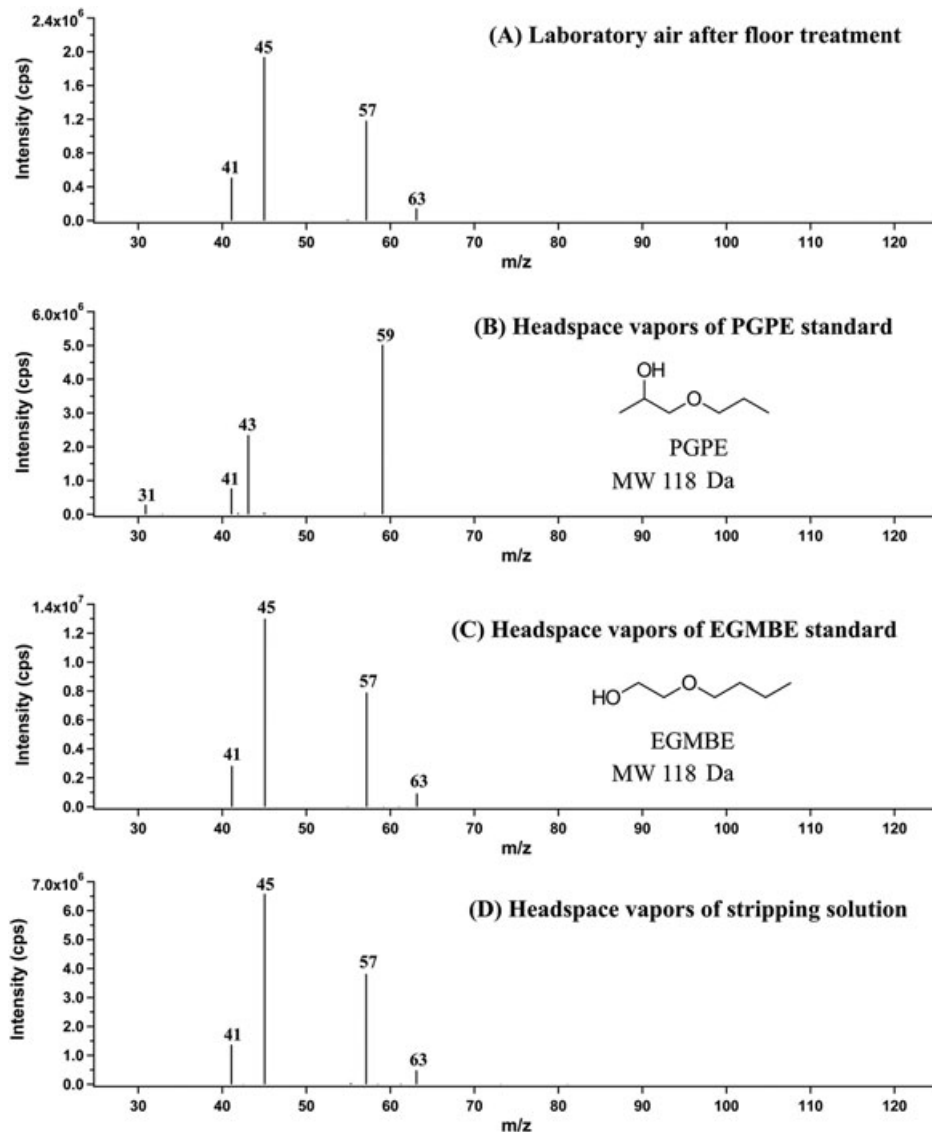
**FIGURE 4** Comparison of EESI-MS/MS(+) product ion spectra of  $m/z$  135 collected at a collision energy of 20 eV for A, laboratory air sampled after floor treatment; B, the headspace of the waxing solution; and C, the headspace of the DEGMEE standard



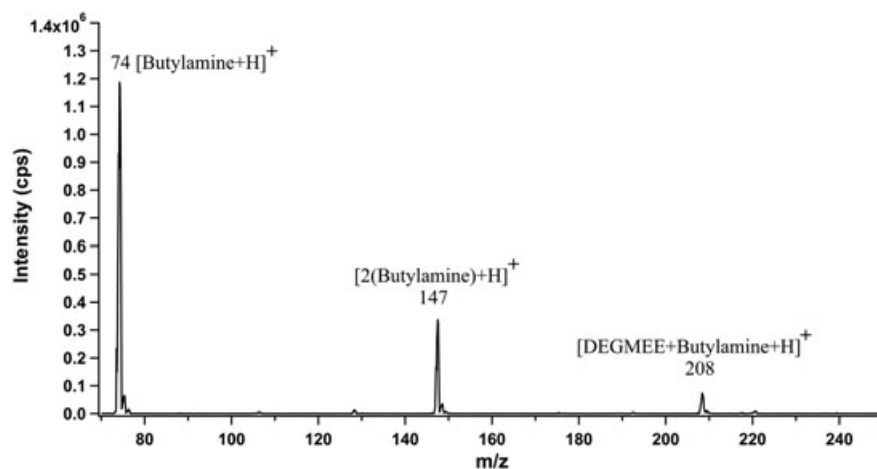
**FIGURE 5** EESI-MS(+) spectra of atomized pentanedioic acid particles  $[(2.2 \pm 0.4) \times 10^6 \text{ particles cm}^{-3}]$ , geometric mean diameter of  $96 \pm 3 \text{ nm}$  ( $\pm 2\sigma$ ) measured A, before and B, after floor treatment. The change in the peak intensities after the floor treatment is well outside the normal  $\pm 20\%$  reproducibility associated with changes in daily alignment and the particle generation process. The intensities are absolute and the top trace is vertically offset for clarity

was confirmed by comparing the solvent-subtracted EESI-MS/MS(+) spectra of the  $m/z$  135 ion in laboratory air (Figure 4A) with that of the same ion in the headspace of the floor waxing solution (Figure 4B) and in the headspace of the authentic DEGMEE standard (Figure 4C). Excellent agreement was observed between all three samples, confirming the identity of this compound and its source as the floor waxing solution. EESI-MS/MS(+) on the  $m/z$  152 ion in all three samples (data not shown) exhibited the same product ions ( $m/z$  135,

89, 73 and 45), providing further confirmation that it is the ammoniated adduct of DEGMEE. Since  $m/z$  152 is due to the presence of ammonia in the wax solution in addition to trace amounts in the laboratory, its signal intensity is higher than that of  $[M+H]^+$  at  $m/z$  135, as seen in Figure 3A. The peaks at  $m/z$  269 and 286 observed in the headspace of the floor waxing solution (Figure 3A) are also seen in the DEGMEE standard (Figure 3B) and are attributed to the  $[2M+H]^+$  and  $[2M+NH_4]^+$  dimer cluster ions of DEGMEE.



**FIGURE 6** Comparison of EESI-MS/MS(+) product ion spectra of  $m/z$  119 collected at a collision energy of 20 eV for A, laboratory air after the floor treatment; B, the headspace of PGPE standard; C, the headspace of EGMBE standard; and D, the headspace of the stripping solution



**FIGURE 7** EESI-MS(+) spectrum of the headspace of liquid *n*-butylamine (MW 73 g mol<sup>-1</sup>) after floor treatment and water rinsing

The peaks at  $m/z$  287 and 304 that appear after floor treatment (Figure 1A) are unidentified. However, we confirmed that these peaks are derived from the compound(s) present in the wax solution, as seen in Figure 3A. It is challenging to identify the compound(s) responsible

for these peaks as the complete composition of the floor wax solution (a proprietary mixture) is not known (e.g. ammonia is not listed in the wax solution). In short, it is clear that all three ambient ionization techniques detected DEGMEE from the floor waxing solution.



It is a common practice when working with ambient ionization techniques to subtract from the spectrum of the analyte the background room air spectrum which may contain contributions from many species. This approach assumes that the background is constant during sample analysis. It also assumes that the background contaminants do not react with the analyte of interest, or cause ion suppression which decreases the analyte signal. However, these assumptions may not always be valid, as shown below.

Significant ion suppression was observed when sampling organic particles by EESI-MS(+). The mass spectrum of pentanedioic acid particles (MW 132 Da) was observed before floor treatment to have peaks at  $m/z$  133 and 115, corresponding to the  $[M + H]^+$  ion and the  $[M + H - H_2O]^+$  fragment ion, respectively. Particles of pentanedioic acid were sampled before and after floor treatment (Figure 5). After the floor treatment, both the  $[M + H]^+$  and  $[M + H - H_2O]^+$  ion signals for pentanedioic acid in EESI-MS(+) were suppressed by more than 75%, as seen in Figure 5B. Similarly, there was significant ion suppression for isopropyl alcohol, as was confirmed in a separate experiment by measuring signals due to isopropyl alcohol vapor in the presence and absence of the headspace of the floor treatment solutions.

As discussed earlier, the signal intensity of an analyte in EESI is dependent on its solubility, concentration and its proton affinity. In the present case, although the solubilities of the glycol ethers and the analytes are similar,<sup>39,67</sup> the proton affinities are significantly different. For example, the proton affinity of isopropyl alcohol is  $793 \text{ kJ mol}^{-1}$ ,<sup>39</sup> lower than those of representative glycol ethers which are in the range  $919\text{--}954 \text{ kJ mol}^{-1}$ .<sup>39</sup> In the case of solid pentanedioic acid, the proton affinity is also lower ( $816 \text{ kJ mol}^{-1}$ )<sup>68</sup> than those of the representative glycol ethers. In addition, extraction from the surface of the pentanedioic acid particles must occur prior to charge transfer, potentially limiting the availability of the analyte. Indeed, Meier et al<sup>31</sup> showed evidence that ionization efficiency is greater for the vapor phase than for liquid droplets. All these factors are consistent with the observed ion suppression of both isopropyl alcohol and pentanedioic acid signals in the presence of the floor emissions.

As can be seen in Figure 5B, a small peak at  $m/z$  119 appears after the floor treatment and is also seen in Figure 1A. Propylene glycol propyl ether (PGPE, MW 118 Da) is listed in the manufacturer's specifications as a component present at 5–10 weight % in the floor stripping solution that was used during the floor treatment to remove stains. However, the EESI-MS/MS(+) spectrum of  $m/z$  119 (Figure 6A) from laboratory air measured after the floor treatment is not consistent with that of an authentic sample of PGPE (Figure 6B). Rather, the EESI-MS/MS(+) spectrum of the  $m/z$  119 ion from an authentic sample of ethylene glycol monobutyl ether (Figure 6C, EGMBE, MW 118 Da) was a better match to both the laboratory air (Figure 6A) and to the headspace of the stripping solution (Figure 6D). This is not surprising as a variety of glycol ethers are used in proprietary cleaning products.<sup>69–73</sup> The peak at  $m/z$  136 (Figure 5B) was attributed to the  $[M + NH_4]^+$  adduct of EGMBE and this was confirmed from its EESI-MS/MS(+) spectrum (data not shown).

A second possible effect of the contaminants in the laboratory air is the formation of new adducts and/or products. For example, a new peak at  $m/z$  208 was observed (Figure 7) in the headspace of liquid *n*-butylamine (MW 73 Da). This peak is assigned to the butylaminium

[DEGMEE + butylamine + H]<sup>+</sup> adduct, and this peak was also observed by DART-MS and PDD plasma MS. Aminium adduct formation is consistent with the proton affinity of *n*-butylamine ( $921.5 \text{ kJ mol}^{-1}$ ),<sup>39</sup> which is higher than that of ammonia ( $853.6 \text{ kJ mol}^{-1}$ ).<sup>39</sup> This highlights some of the challenges in applying open-air ionization techniques in which trace VOC concentrations can be higher than in closed ionization sources.

## 4 | CONCLUSIONS

Ambient ionization techniques are useful as they are sensitive, experimentally straightforward and require minimal sample preparation. However, as demonstrated in the current study, organic compounds released by activities in the vicinity of the instrument can cause ion suppression and/or the appearance of new peaks. Although this study used positive ion mode to identify the possible issues with ambient ionization techniques, it should be noted that these effects can also occur in negative ion mode.<sup>24</sup> The glycol ethers identified in this study are found in many cleaning products.<sup>69–73</sup> In other situations, there may be different interfering species involved, but, in any event, caution should be exercised when activities in the surroundings cause changes in the background spectrum. This drawback of ambient air contaminants is substantially outweighed by the versatility and simplicity of ambient ionization mass spectrometry techniques.

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